Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

AD-A265 293

REPORT DOCUMENTATION PAGE

Approved No 0704 0188

1a REPORT SECURITY CLASSIFICATION Unclassified	
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; distribution unlimited.
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Report #20	5 MONITORING ORGANIZATION REPORT NUMBER(S) 4135010
6a NAME OF PERFORMING ORGANIZATION University of Minnesota; 6b OFFICE SYMBOL (If applicable) ONR	7a NAME OF MONITORING ORGANIZATION Office of Naval Research
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry, 207 Pleasant St. SE, Minneapolis, MN 55455-0431	7b ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street, Arlington, VA 22217-5000
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research; 8b OFFICE SYMBOL (If applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N001489J1301
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street, Arlington, VA 2217-5000	10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
61153N	4135		4135010

11 TITLE (Include Security Classification)
"Solid-State Structures of Guanidinium Methane-, Ethane-, and Trifluoromethane-sulfonate" (Unclassified)

12 PERSONAL AUTHOR(S)
Russell, V.A.; Etter, M.C.; Ward, M.D.

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM 6/1/92 TO 5/31/93	April 22, 1993	7

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	guanidinium sulfonate/hydrogen bonding/ molecular crystal
07	03		

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The solid-state structures of guanidinium sulfonates, $[C(NH_2)_3]^+RSO_3^-$, are being studied and the role of hydrogen bonding in controlling molecular packing assessed. We have found that guanidinium sulfonates frequently self-assemble into two-dimensional sheets formed by hydrogen bonds between the six guanidinium protons and the six sulfonate oxygen lone electron pairs. X-ray structures of guanidinium methanesulfonate, guanidinium ethanesulfonate, and guanidinium triflate are reported here. Each of these salts crystallizes in a bilayer structure of hydrogen-bonded sheets.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Harold E. Guard	22b TELEPHONE (Include Area Code) (202) 696-4311; 22c OFFICE SYMBOL ONR Code 1113

DD Form 1473, JUN 86 Previous editions are obsolete
SECURITY CLASSIFICATION OF THIS PAGE
S/N 0102-LF-014-6603 Unclassified

OFFICE OF NAVAL RESEARCH

Grant or Contract N001489J1301

R&T Code 4135010

Technical Report #20

"Solid-State Structures of Guanidinium Methane-, Ethane-, and Trifluoromethanesulfonate"

by

V.A. Russell, M.C. Etter, and M.D. Ward

University of Minnesota
Department of Chemistry
Minneapolis, MN

April 22, 1993

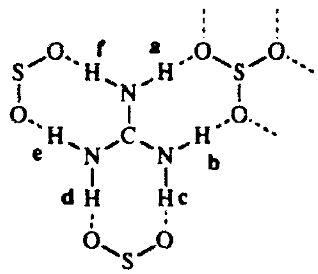
Control of packing in the solid-state is instrumental in the design of molecular materials. Hydrogen bonds, one of strongest intermolecular interactions, can be used to direct crystal packing. We have discovered that guanidinium sulfonates, $[C(NH_2)_3]^+$ RSO_3^-, frequently pack by forming two-dimensional sheets of hydrogen bonds between the six guanidinium protons and the six sulfonate oxygen lone electron pairs (Figure 1). This is important for materials design because crystal packing is strongly and reproducibly controlled in two dimensions. Guanidinium methanesulfonate and guanidinium ethanesulfonate are isostructural and crystallize in monoclinic space group *C2/m*. Guanidinium trifluoromethanesulfonate (triflate) has a similar structure, but crystallizes in monoclinic space group *C2/c*. Crystallographic data for the three salts is given in Table I.

Table I. Crystallographic Data for Guanidinium Salts of Methanesulfonate, Ethanesulfonate, and Triflate.

compound	guanidinium methanesulfonate	guanidinium ethanesulfonate	guanidinium triflate
formula	$C_2H_9N_3O_3S$	$C_3H_{11}N_3O_3S$	$C_2H_6F_3N_3O_3S$
FW	155.17	169.20	209.14
crystal color, habit	col, plate	col, plate	col, plate
crystal size (mm)	0.700 x 0.500 x 0.100	0.550 x 0.450 x 0.170	0.550 x 0.450 x 0.150
crystal system	monoclinic	monoclinic	monoclinic
space group	*C2/m*	*C2/m*	*C2/c*
a (Å)	12.778 (5)	12.793 (4)	12.988 (7)
b (Å)	7.342 (2)	7.398 (5)	7.512 (2)
c (Å)	9.998 (2)	11.172 (3)	18.45 (1)
β (°)	126.96 (2)	128.060 (2)	111.69 (4)
V (Å^3)	749.6 (8)	833 (1)	1672 (3)
Z	4	4	8
D_x (g/cm^3)	1.375	1.350	1.661
F (000)	328	360	848
μ (MoKα) (cm^{-1})	3.66	3.35	3.99
T (°C)	24	24	24
no. data ($F_o>2\sigma(F_o)$)	743	749	1284
R	0.051	0.058	0.038
R_w	0.079	0.072	0.053
$2\theta_{max}$ (°)	51.9	56.0	51.9
range of *hkl*	±15, +9, ±12	±16, +9, ±14	±12, +7, ±17
$(shift/error)_{max}$	0.02	0.02	0.04
largest peak (e$^-$/Å^3)	0.48	0.33	0.28
GOF	2.33	1.50	1.36

Each structure is composed of two-dimensional guanidinium-sulfonate hydrogen-bonded sheets in approximately the *ab* plane. The N...O distances of the hydrogen bonds are given in Table II. Figure 2 shows a view normal to the guanidinium ions of one hydrogen-bonded layer in guanidinium methanesulfonate; analogous packing occurs in the guanidinium salts of ethanesulfonate and triflate. The hydrogen-bond sheets pack in bilayer structures (Figure 3) in which the sulfonate R groups (methyl, ethyl, or trifluoromethyl) are all oriented to one side of each sheet, resulting in partitioning into hydrophobic and hydrophilic regions. Guanidinium ethanesulfonate is isostructural to guanidinium methanesulfonate; the cell parameters *a*, *b*, and β are equivalent to those in guanidinium methanesulfonate, with the *c* constant (direction approximately normal to the hydrogen-bond sheet) lengthening (11.172 versus 9.998 Å) to accomodate packing of the slightly larger ethyl group. Guanidinium triflate packs slightly differently; the mirror symmetry element is replaced by a glide in this structure. We believe that the difference in packing arises from an electronic effect due to the fluorine atoms of the triflate. The controlled crystal packing in two dimensions in these salts suggests that further engineering in the third dimension with lead to new materials with desirable properties such as second-order nonlinear optical activity.

Table II. N...O Distances (Å) in guanidinium methanesulfonate, ethanesulfonate, and triflate.



hydrogen bond	guanidinium methanesulfonate	guanidinium ethanesulfonate	guanidinium triflate
a	2.893 (2)	2.927 (3)	2.985 (4)
b	2.917 (3)	2.957 (4)	2.990 (4)
c	2.935 (3)	2.957 (3)	2.986 (3)
d	= c	= c	2.992 (3)
e	= b	= b	2.998 (3)
f	= a	= a	3.001 (3)

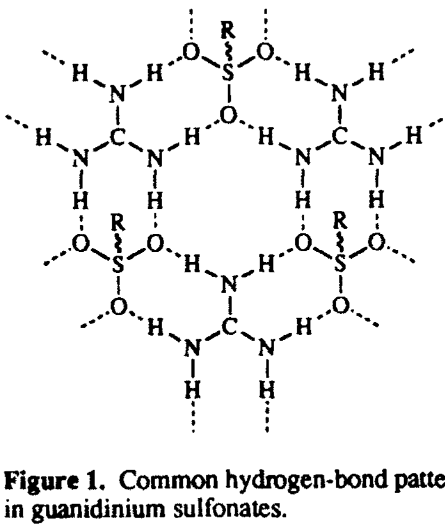


Figure 1. Common hydrogen-bond pattern in guanidinium sulfonates.

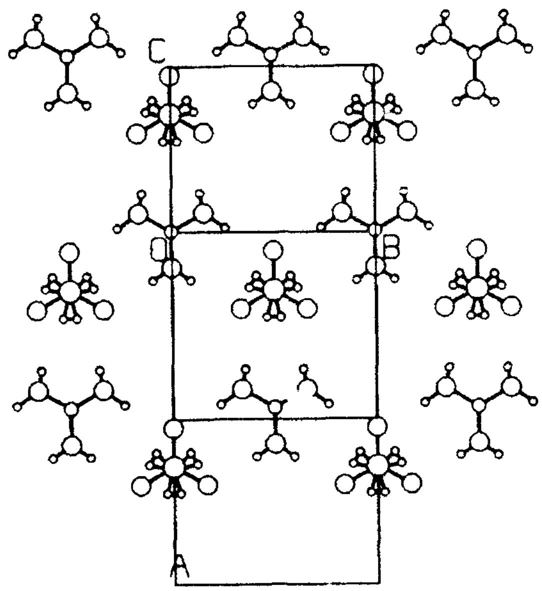


Figure 2. View normal to guanidinium ions of one hydrogen-bond layer in guanidinium methanesulfonate.

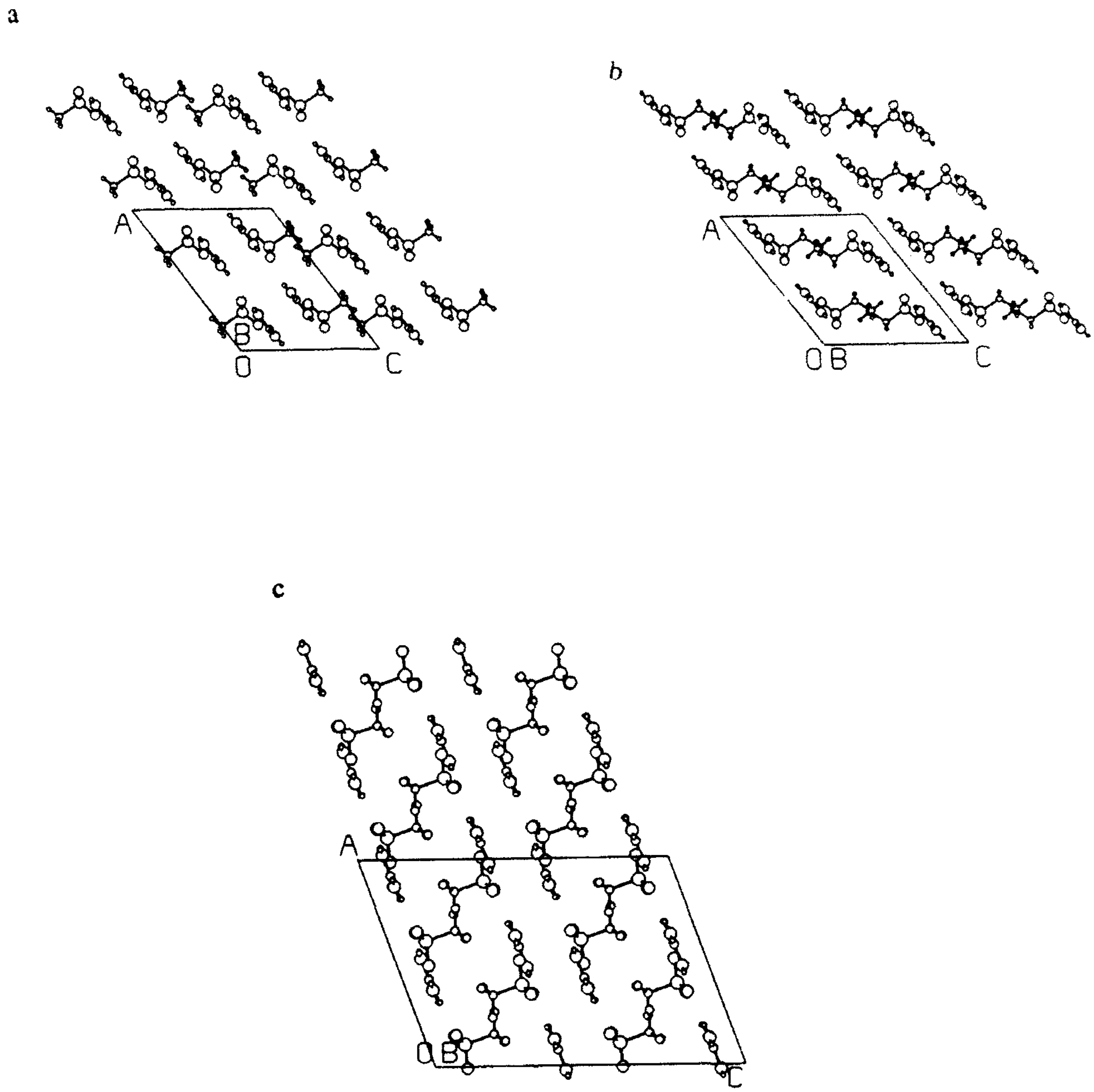


Figure 3. Bilayer structures in (a) guanidinium methanesulfonate, (b) guanidinium ethanesulfonate, and (c) guanidinium triflate.

Professor O.T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Alan Berry
Chemistry Division, Code 6120
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5000

Professor Jerald S. Bradshaw
Department of Chemistry
Brigham Young University
Provo, UT 84602
R&T Code 413p002

Professor Ronald Breslow
Department of Chemistry
Columbia University
New York, NY 10027
R&T Code 413p005

Dr. Duncan W. Brown
Advanced Technology Materials, Inc.
520-B Danbury Road
New Milford, CT 06776

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907

Professor Steven L. Buchwald
Department of Chemistry
Massachusetts Institute of Tech
Cambridge, MA 02139

Professor Cynthia J. Burrows
Department of Chemistry
State University of New York at
Stony Brook
Stony Brook, NY 11794-3400

Dr. Roque J. Calvo
Executive Secretary
The Electrochemical Society
10 South Main Street
Pennington, NJ 08534-2896

Professor Peter Chen
Department of Chemistry
Harvard University
Cambridge, MA 02138

Professor N. John Cooper
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Professor Anthony W. Czarnik
Department of Chemistry
Ohio State University
120 West 18th Avenue
Columbus, OH 43210-1173

Professor Peter Dervan
Department of Chemistry
California Institute of Technology
Pasadena, CA 91125

Professor Francois N. Diederich
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles, CA 90024

Professor Dennis A. Dougherty
Department of Chemistry
California Institute of Technology
Pasadena, CA 91125

Professor Kenneth M. Doxsee
Department of Chemistry
University of Oregon
Eugene, OR 97403

Dr. Regis J. Ebner, Jr.
Director of Finance
Materials Research Society
9800 McKnight Road, Suite #27
Pittsburgh, PA 15237

Professor Margaret C. Etter
Department of Chemistry
University of Minnesota
207 Pleasant Street, S.E.
Minneapolis, MN 55455

Professor Wilmer K. Fife
Department of Chemistry
Indiana University
1125 East 38th Street
P.O. Box 647
Indianapolis, IN 46223

Professor Samuel H. Gellman
Department of Chemistry
University of Wisconsin
Madison, WI 53706

Professor Andrew D. Hamilton
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Prof. Maık J. Hampden-Smith
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. Kelvin Higa
Chemistry Division
Research Department
Naval Weapons Center
China Lake, CA 93555

Professor Kenneth D. Karlin
Merryman Hall 146
The Johns Hopkins University
34th & Charles Streets
Baltimore, MD 21218

Professor Arthur E. Martell
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

Professor Thomas J. McCarthy
Department of Polymer Science
University of Massachusetts
Room 701 Graduate Research Center
Amherst, MA 01003
R&T Code 400x015

Dr. Stephen W. McElvany
Code 6113, Chemistry Division
Naval Research Laboratory
Washington, DC 20375-5000

Professor Lisa McElwee-White
Department of Chemistry
The Leland Stanford Junior Univ.
Stanford, CA 94305

Professor Theordore G. Pavlopoulos
Naval Ocean Systems Center
Code 521 (B-111)
San Diego, CA 92152-5000

Professor William S. Rees, Jr.
Chemistry Division
The Florida State University
Tallahassee, FL 32306-3006

Professor Peter Schultz
Department of Chemistry
University of California
Berkeley, CA 94720
R&T Code 413j005

Dr. Alok Singh
Ctr. for Bio/Molec. Science Eng.
Department of the Navy
Naval Research Lab., Code 6090
Washingotn, DC 20375-5000

Dr. Michael L. Sinnott
Unviersity of Brisol
School of Chemistry
Cantock's Close
Briston, England BS8 1TS

Dr. Timothy M. Swager
Departmentof Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706

Professor Jeffrey D. Winkler
Department of Chemistry
The University of Chicago
5735 S. Ellis Avenue
Chicago, IL 60637

Professor Jeffrey D. Zubkowski
Department of Chemistry
Jackson State University
P.O. Box 17910, 1400 Lynch St.
Jackson, MS 39217